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APPLIED HYDROGEN-ION CONCENTRATION—A STUDY OF ITS MERITS IN PRACTICAL FILTER PLANT OPERATION

By A. Wagner[1] and Linn H. Enslow[1]

During the past year there has appeared in the literature considerable new thought concerning water purification and sewage treatment.

The writings of Wolman and Hannan[2] and of Massink and Heymann[3] contained such information as to warrant an investigation into the merits of pH application to the control of coagulation at the various filter plants in Virginia, as a practical means of solving coagulation difficulties or of increasing plant efficiency in other ways.

The technique of pH observations is of such simplicity and the apparatus required so easily manipulated as to make the adoption of routine pH observations appear desirable. The only remaining question in the authors' minds was: "Are we justified in advising the adoption of pH observations as routine at any plant, until we have made a study of its merits where applied to waters of the character handled in Virginia? If the tests are applicable what may we offer the prospective users of the "new" test as a good and logical reason why they should employ them and, more important, when, where and how often should they be made, if used as a routine control test?"

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[1] State Department of Health of Virginia, Richmond, Va.

[2] "Residual aluminum compounds in filter effluents," Chemical and Metallurgical Engineering, vol. 24, no. 17, April 27, 1921.

"Further observations on pH in natural waters," Chemical and Metallurgical Engineering, vol. 25, no. 11, September 14, 1921.

[3] "Significance of pH in drinking water and particularly for the business of water supply," Journal, vol. 8, no. 3, May, 1921.

In order to answer these questions to our satisfaction, an investigation was begun with the idea of testing Tillman's formula, slightly modified by the authors, as a means of calculating the pH, CO_2 or alkalinity content of waters, when any two of the three members have been determined from observation or titration. The second and really important matter to investigate was that of operation economics. *Could we reduce the alum bill and at the same time improve the qualtiy of filtered water?* After improving the quality of the filtered water could we improve the chemical and physical quality of the water as delivered to the consumer, by removing or absorbing a portion of the free carbon-dioxide from the filtered water? In other words, was it practical to remove a portion if not all of the free CO_2 from the water in the clear well, thereby reducing its corrosive quality. As a result of such treatment would there be a reduction of consumers' complaints in direct proportion to the reduction of "aggressivity" of the water in the mains and of "red-water" at the taps? In the belief that all of the questions could be answered in the affirmative, the authors undertook to prove it through the aid of the pH measurements, as an added method of plant-control.

It might be well at this point to explain why the recent ideas of coagulation-control through pH regulation of the coagulated-water appealed so much to the writers. Having been in charge of water purification at various plants in the past, practical experience had demonstrated that the following conclusions are valid.

1. That waters aerated even immediately after alum had been added were slower to coagulate properly than when aeration was not resorted to—organic waters of low alkalinity excepted.
2. That certain waters required the addition of artificial alkalinity during coagulation. In such cases better coagulation and more effective color-removal could be had by withholding the alkali addition until the water had reached a point in the settling-basins as near to the filters as was practical for the production of a satisfactory applied water.
3. That in any event a very careful control of the alkali addition was required to avoid the so-called "setting of organic color" or

the production of a "milky" effluent. To avoid these undesirable conditions an alkali dose was required of such proportion that the alkalinity of the applied water should vary but little. This "alkalinity zone." within the limits of which a satisfactory applied water resulted, was narrow. It was necessary to maintain an alkalinity of applied water not higher than 3 to 5 parts below that of the raw-water and often considerably less. If the alkalinity was not kept up in the "zone" having a maximum variation of about 6 p.p.m. alkalinity, troubles would ensue. Too low alkalinity with high free CO_2 meant a floc of poor settling quality and also the air-binding of filters by CO_2. Too high an alkalinity meant a "setting of the color" and "milky" filtrate containing aluminum compounds. All three qualities we now believe to have been due to solution of or possibly the "peptization" of the alumina "floc," with the resulting release of adsorbed coloring matter and the passage of both through the sand bed. Too great an alkalinity will furthermore in some cases tend to peptize or dissolve the "mat" already on the sand-bed and also the film which always surrounds the sand grains. An old custom now discarded, was to clean the filter sand-bed of mechanical filters at regular intervals by allowing a dilute soda-ash solution to remain in contact with the dirty sand for some hours and later sterilize the bed with live steam. Such practice was abandoned because filters produced poorer bacterial results after such treatment than prior to it. The probable explanation lies in the fact that the "films" were peptized or dissolved and thereby removed from the sand. After such treatment there was probably insufficient "coagulum" remaining in the filter tub to form an effective "mat" after washing with filtered water. The bacteria therefore literally "slipped" over the sand grain surfaces and through the filter-bed.

4. Operation of certain plants treating river waters which would vary in alkalinity, color and turbidity with seasonal changes always ran into coagulation difficulties, necessitating a relatively high alum dose whenever the alkalinity ascended to 80 p.p.m. with attending low CO_2 and turbidity content. It was apparent that most of the difficulty could not be atrributed to the low turbidity, since this was often very low when the alkalinity was 40 to 60 p.p.m. and with a CO_2 content of 2 to 4 p.p.m. It appeared that some means was necessary to reduce the alkalinity. This was being accomplished through the certain but expensive method of adding more alum to the water. No real thought had been given to the rôle played by

the CO_2 content in such instances. Now we believe that the larger alum dose was acting as "pH reducer" through an alkalinity reduction and CO_2 increase, both or either of which accomplishments would serve the purpose of producing the so-called "optimum point" of coagulation or preparing the "pH zone" in which satisfactory coagulation results.

It is our intent to make further investigations of such waters during the next fall at which time the alkalinity rises. An attempt will be made to produce the proper "pH zone" or obtain the "optimum point" for proper coagulation through addition of a small quantity of sulphuric acid to the alum solution or perhaps by gassing the raw-water in the mixing chamber with CO_2, making use of liquid CO_2 in cylinders and applying it through large diffusers. In the limestone section of Virginia are streams of high alkalinity (200 p.p.m.) and low CO_2 content. Some are being considered as sources for future filter plants. Investigation of coagulation of such waters will be made by the writers in the immediate future.

5. During the past two years, duty has carried us to many different filter plants where we have met with a variety of waters of varying qualities. Experience has shown us that where artificial alkalinity addition is necessary the following "laws of coagulation" *must* be "enforced" in this state:

a. In no case allow the alkalinity of the treated water to exceed that of the raw-water. Cases of exceptionally high CO_2 content of un-aerated raw-water are excepted.

b. If free CO_2 in the filter effluent is of sufficient concentration as to cause serious red-water troubles, CO_2 must not be absorbed by alkali addition prior to filtration even though such is added to the filter influent chamber.

c. In cases where the CO_2 content of a filtered water must be reduced, this shall be accomplished by aeration of the filtered-water or absorption of the CO_2 by alkali prior to pumping into the mains.

From the above it is readily seen that we were headed in the direction of obtaining efficient filtration, although the scientific reasons were not known to us. Upon the appearance of the first article by Wolman and Hannan, pointing to the rôle played by pH in coagulation and settling of waters, there was one thing definitely apparent. The thought that it must necessarily be pH which was to direct our future procedure of scientific coagulation control found a fertile field and, therefore, the authors undertook the preliminary investigation of the matter which is the subject of this article. The incentive furnished by Wolman and Hannan has led us to certain valuable knowledge regarding pH determination, its theory and its practical value. What is of more importance however, is that economy of alum use and the abatement of the red water nuisance have resulted from the study. Credit for the elimination of red water, we acknowledge to Massink and Heymann for the original and to Wolman and Hannan for their industry in causing its publication in available form. We hope that our endeavors may result in a slight addition to the data already published and that this article may be of value to others who are giving thought to the question of pH and its merits in the practical field of filtration.

METHODS PURSUED IN THE INVESTIGATION

Ampules of pH color standards and indicator solutions were obtained from the La Motte Chemical Company of Baltimore. Each author having a complete set and a field kit fitted for making CO_2 and alkalinity determinations, various plants were visited and readings of alkalinity, CO_2 and pH were made. Several plants were re-visited in some cases as many as four times for the purpose of obtaining varied conditions at the plant.

Having obtained the required data on existing raw, coagulated and filtered waters, experiments were made along the lines of varying the alum or alkali dose, in each instance taking readings and recording the quality of "floc" and its behavior. Changes in the point of application of alkali also were made. At some plants it was discontinued in the raw water and applied first to the filter influent and later discontinued at this point and application made instead to the filter effluent. At other points it was necessary to apply a portion of the alkali to the raw water. The alkali dose was increased by degrees, readings made and observations noted. The dose was then increased to a point where the "floc" was destroyed. From this point it was again lowered until the most satisfactory "floc" in the series was obtained. In some cases "jar" tests were made at the plant. This was done only where it was impossible without considerable trouble to the personnel operating the plant and expense to the municipality, to have equipment for alkali feed put in or the existing location changed.

The experiments were carried out using raw water and varying combinations of alum, soda-ash, limewater, finely ground limestone, finely ground sand and sulphuric acid. These experiments are interesting from the standpoint of the investigation, but since this paper is intended primarily to cover actual operating conditions, as existed or were created, at the various plants and as a means of testing the merits of pH control and Tillman's formula, we will not attempt to describe in detail the jar experiments. We shall outline the results from these experiments, touching on the principal points and only include in tables presented the measurements and data as obtained from actual plant operation.

In the jar experiments ½ gallon of raw water was taken. Prepared solutions of known strength carried in the kit were used to create the desired combination of chemical doses.

The results obtained indicate:

1. Where alkali is added in coagulation, the "floc" is materially hurt as soon as pH 7 is exceeded and at pH 7.3 little if any coagulation results.

2. Most satisfactory coagulation was obtained in the pH zone 6.5 to 7 for the non-organic waters. For organic waters the pH zone extended as low as 5.7 pH but never above 6.5 pH.

3. Such waters as were experimented with required no acid addition to improve coagulation. The addition of acid produced inferior coagulation even though the pH was 6.65 for the coagulated water.

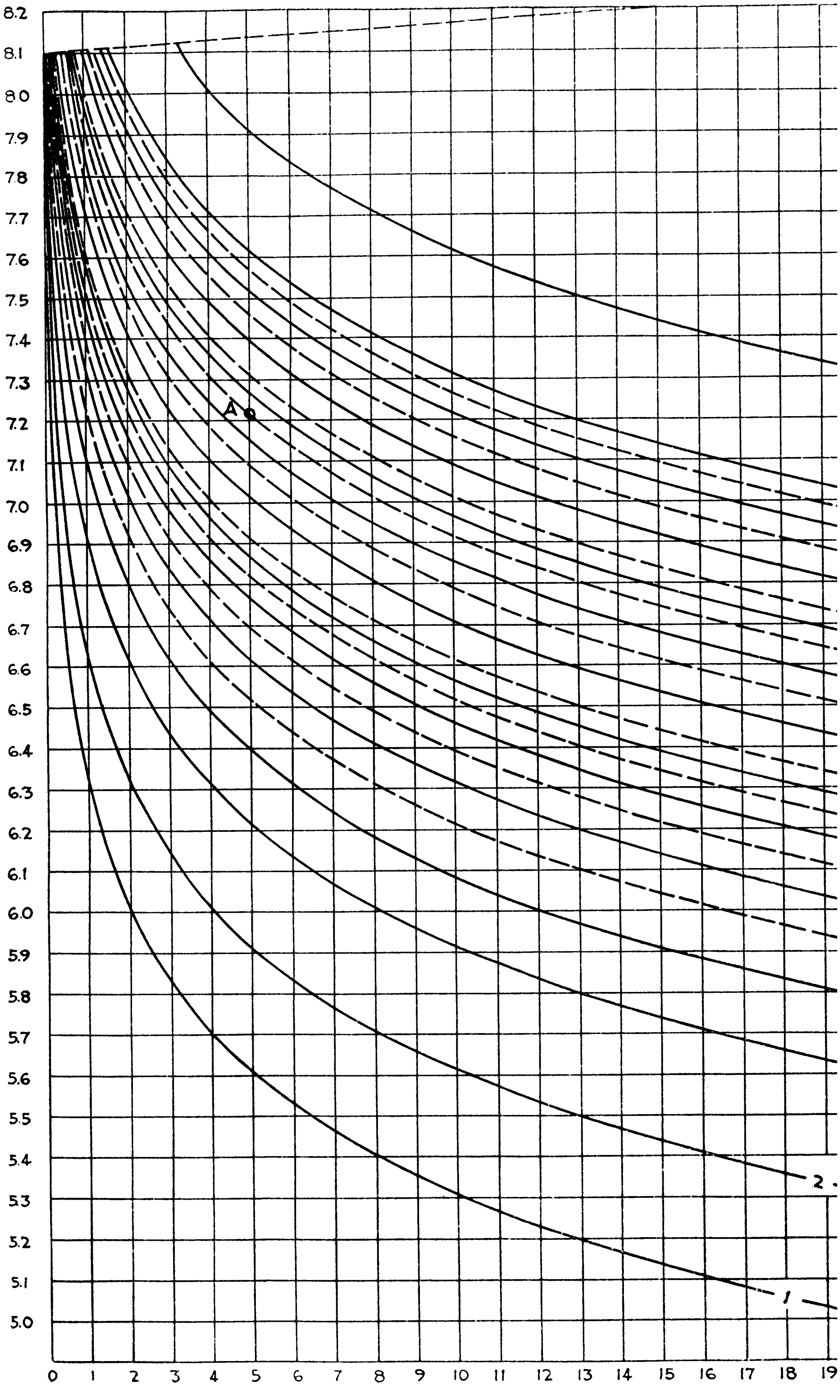
Note: The pH of raw water was 7.5, but 2.5 grains per gallon of alum produced a good "floc" with resulting pH of 6.8. The alkalinity of the raw water was only 41 and CO_2 content, 2 parts. Waters of higher alkalinities and low CO_2 *may* be benefited through acid addition.

4. Addition of finely ground limestone during coagulation, followed by a two-minute vigorous mixing, always produced an improved "floc" and more effective settling.

Note: Limestone apparently had very little effect chemically. CO_2 was only one part less and alkalinity only two parts more in the coagulated water to which limestone had been added just prior to alum addition than was the case with coagulated water receiving the same alum dose but no limestone. There was an increase in pH from 6.1 to 6.3 or only 0.2 in the limestone treated water.

5. Finely pulverized cinders or sand added during coagulation, followed by a two-minute vigorous mixing, produced an improved "floc" and more effective settling.

Note: The "floc" produced by grit addition was equally as good if not superior to that produced by limestone and also superior to


8.2
8.1
8.0
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7.8
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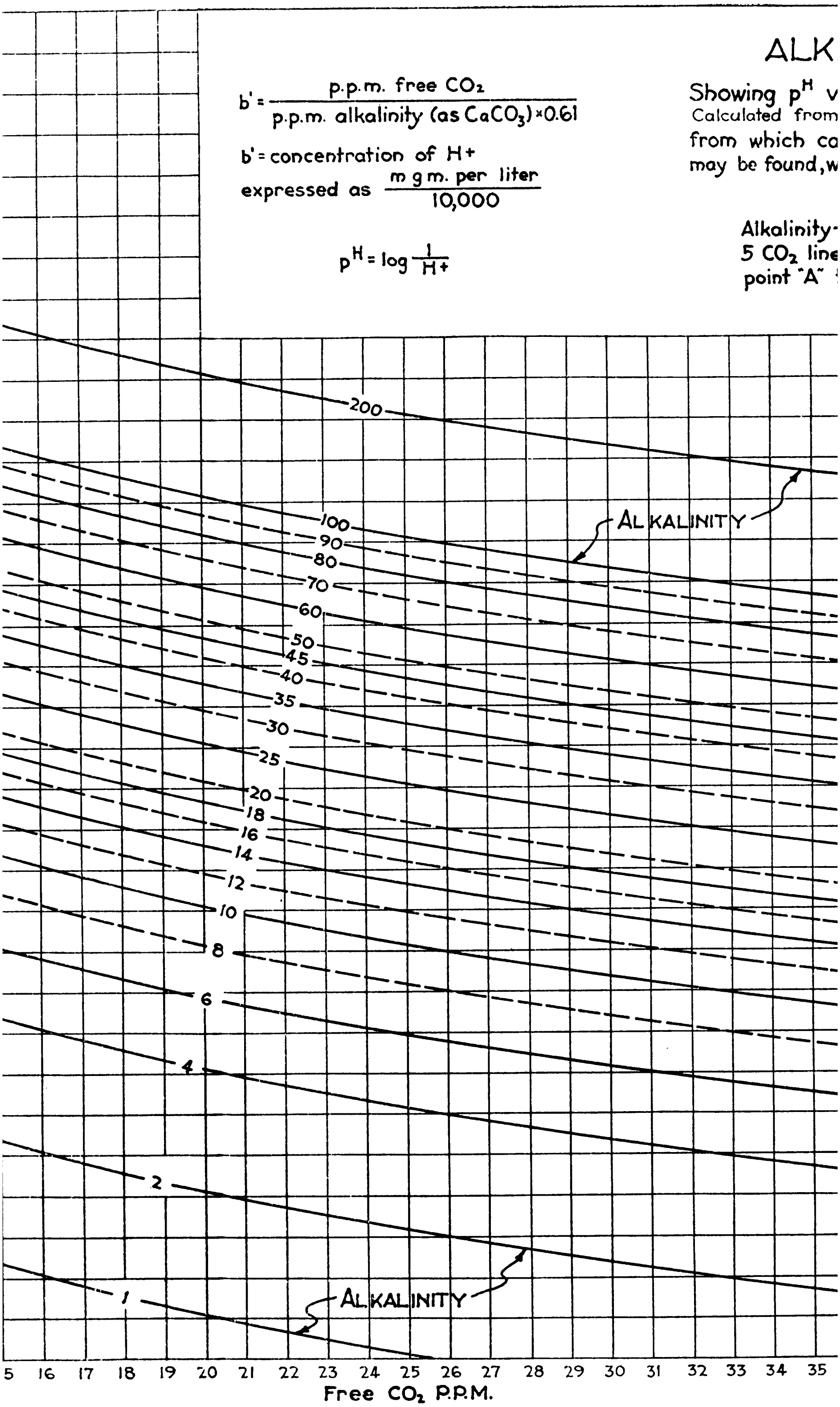


$$b' = \frac{\text{p.p.m. free } CO_2}{\text{p.p.m. alkalinity (as } CaCO_3) \times 0.61}$$

b' = concentration of H^+ expressed as $\frac{\text{m g m. per liter}}{10{,}000}$

$$p^H = \log \frac{1}{H^+}$$

Fig. 1

ALKALINITY CURVES

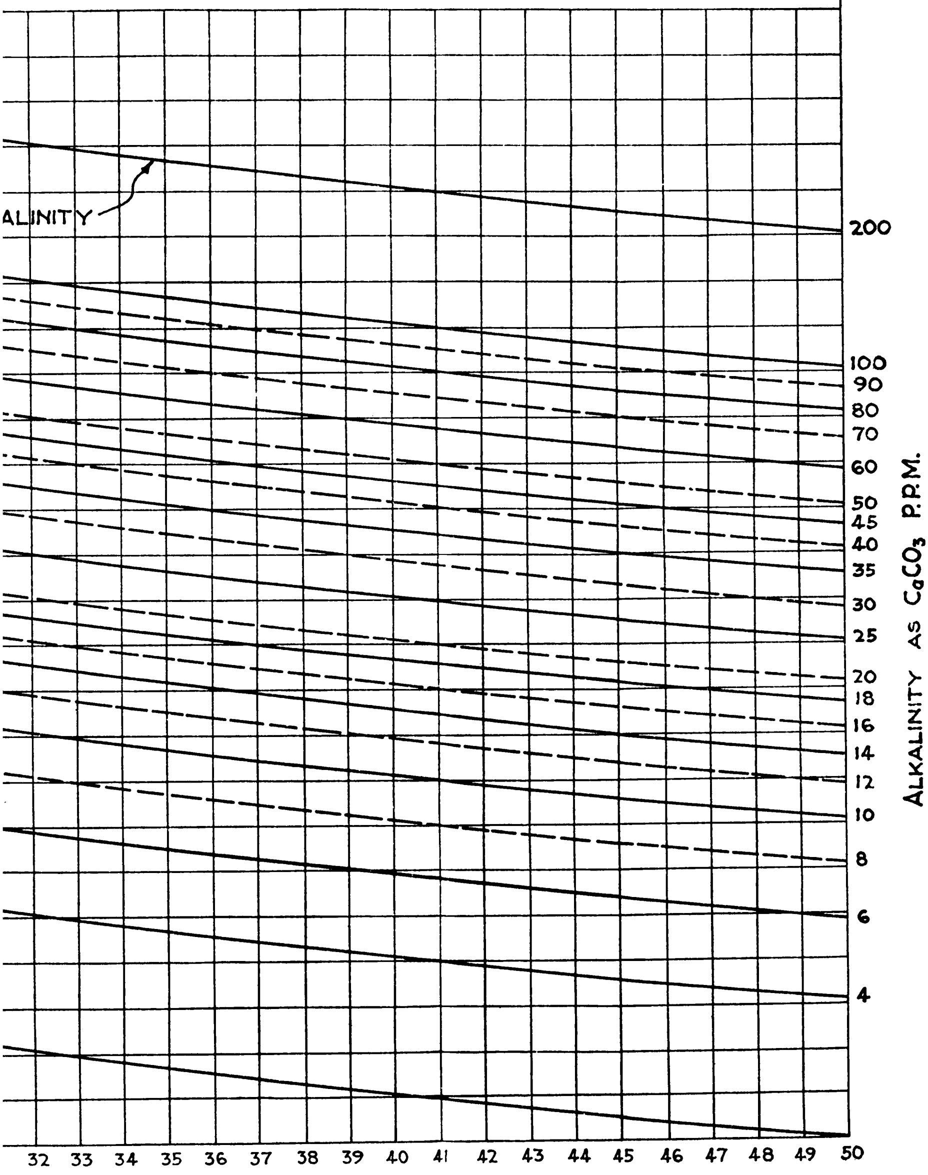
* * *

Showing p^H value for CO_2 content 0 to 50 p.p.m.
Calculated from "Tillman's" formula by A. Wagner
from which calculated alkalinity, CO_2, and p^H concentration may be found, when any two of the three factors are known

* * *

Example

Alkalinity-40 p.p.m. CO_2-5 p.p.m. to find p^H
5 CO_2 line & 40 alkalinity curve intersect at point "A" taking horizontal line to left p^H= 7.21



any alum dose alone or combination of alkali and alum, except in instances where sufficient alkalinity did not exist in the raw water to furnish the required hydroxyl-ions to combine with the alum added and completely to decompose it.

THE TESTING OF TILLMAN'S FORMULA AND ANALYSIS OF DATA

The first step was the preparation of figure 1. This chart was prepared through use of Tillman's formula for calculating the theoretical pH of waters containing only bi-carbonate alkalinity and carbon-dioxide from zero upwards.

$$^{*}(1) \quad h^{\cdot} = \frac{(\text{p.p.m. free } CO_2) \times 3}{(\text{p.p.m. bi-carbonate alkalinity expressed as } CaCO_3) \times 0.61}$$

$$(2) \quad h^{\cdot} = \frac{H+}{10^{-7}} \qquad (3)\ H+ = h^{\cdot} \times 10^{-7} \qquad (4)\ pH = \log \frac{1}{H+}$$

$$^{*}h^{\cdot} = \text{concentration of } H^{+} \text{ expressed as } \frac{(\text{mgm. per liter})}{10{,}000.}.$$

To prepare these curves, each alkalinity shown was taken with each CO_2 content shown. The pH was calculated, the points were plotted and then the curves were drawn through them. (Fig. 1.)

Having completed the chart it was then tested at several points in the following manner:

The alkalinity, CO_2 content and pH were carefully determined on a filtered-water. Using alkalinity and CO_2, the theoretical pH, as found from the curve, checked with the pH observed within the limit of error of observations. Using this same water and artificially varying its CO_2 content and alkalinity, further observations and checking were carried out. The final alkalinity was 162 p.p.m. with a CO_2 content of zero. Tillman had claimed accuracy of the formula only where the ratio of free CO_2 to alkalinity is not less than 1 p.p.m. CO_2 to each 65 p.p.m. alkalinity, and therefore as expected the pH as found from the curve was materially higher than that observed, as soon as this ratio no longer held. For example, an alkalinity of 55 (all bicarbonate) and CO_2 of 0 when using the chart indicates a theoretical pH of about 9, whereas the observed pH was 8.1.[4] The alkalinity of 162 (all bicarbonate) and CO_2 of zero from the chart indicates a theoretical pH of about 9.53, whereas the observed pH was 8.1.[4] We have discontinued on this account the alkalinity curves at points on their upward swing above which, if used, they would be plainly in error. We cannot claim that the curves are perfect even yet, but for all practical purposes they are extremely serviceable, as will be shown later. For the purpose of pointing out under what conditions the greatest inaccuracy may be expected, when the chart is used to arrive at an unknown—the two other quantities necessary having been observed—the following is stated:

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[4] From laboratory observations it would appear that a trace of normal carbonate alkalinity irrespective of bi-carbonate alkalinity produces pH 8.1 according to the pH standards purchased, which were prepared from phenol red up to pH 8.4.

1. *Concerning bi-carbonate waters of any alkalinity and varying CO_2 content.* An error of 1 p.p.m. in CO_2 titration will cause an error of calculated pH of from only 0.05 at 10 p.p.m. CO_2 to as much as 0.3 at 1 p.p.m. CO_2. Within the CO_2 range 1 to 0 a fractional p.p.m. CO_2 error will result in even greater error of calculated pH.

2. *Concerning bi-carbonate waters of any CO_2 content and varying degree of alkalinity.* An error of 1 p.p.m. in alkalinity titration will cause an error of calculated pH of as much as 0.3 in waters of 1 p.p.m. alkalinity, whereas an error in pH of only 0.02 would result from an error of as much as 5 p.p.m. titrated alkalinity in waters of 100 p.p.m. alkalinity.

As a result of the above, the following conclusions relating to the use of the chart, where accuracy is desired, are set forth.

1. *Concerning waters of bicarbonate alkalinity of 5 or less.* *a.* When CO_2 is less than 6 p.p.m., observe the pH, titrate the alkalinity and locate the calculated CO_2 content.

b. When CO_2 is greater than 6 p.p.m., observe the pH, titrate the CO_2 carefully and locate the calculated alkalinity, or titrate the alkalinity and CO_2 and locate the calculated pH.

2. *Concerning waters of bi-carbonate alkalinity greater than 5.* *a.* When CO_2 is less than 10 p.p.m., titrate the alkalinity, observe the pH and locate the calculated CO_2 content.

b. When CO_2 is greater than 10 p.p.m., titrate the alkalinity, and observe the pH, or locate the calculated pH after titrating the CO_2. Both methods are of like accuracy.

3. *Concerning bi-carbonate waters of any alkalinity and CO_2 less than 1.* Observe pH, titrate alkalinity and locate the calculated CO_2.

Note: Whenever the proportion of CO_2 is less than 1 p.p.m. for each 65 p.p.m. of alkalinity present the accuracy of calculated pH is materially affected—always being greater than that observed.

ANALYSIS OF FILTER PLANT DATA

Having collected the desired data at fourteen plants and at several under different conditions of the water being treated, the next step was that of analyzing these data. Table 1 was prepared for this purpose. The observed pH, CO_2 and alkalinity of each test are recorded in columns (O) indicating observed values. In the column (C)—one to the right under each heading—were placed the values found through the use of figure 1 or, in other words, theoretical values, assuming the two other factors to have been correctly determined in the actual observations and titrations.

Seeing that a good portion of the observed values failed to check with the calculated it was decided to divide the table into sections A and B. In section B were placed all tests wherein calculated and observed pH values differ by more than pH 0.10. This particular degree of variation was chosen because we believe such a difference to be of no consequence in the practical application of the chart for ascertaining the pH of a particular water in filter-plant control, unless it should happen to hit about pH 7 or 7.1 at which point 0.1 pH is of moment in coagulation of non-organic waters.

Upon examining table 1 it will be seen that 62 of the 95 tests fall in section A, and 33 fall in section B, which is equivalent to saying that 65 per cent of the samples showed calculated values comparing favorably with observed values, whereas 35 per cent failed to agree by less than 0.10 pH.

For convenience we show in table 2 the various plants and the proportion of tests made at each which fall within the satisfactory range. Above the line are plants which have more than 60 per cent of tests falling in section A, and below the line those which have the majority of tests in section B. If we are allowed to eliminate the two Bedford tests and the one Hopewell test, which we admit are not of much value because of the small number and the lack of tests on treated water in one and raw water in the other, we will then have only two plants of the fourteen in which there is an indication of the material failure of application of calculated values for pH, etc., as compared with the observed values. At present we have no adequate explanation as to why Norfolk and Petersburg fail to fall in the satisfactory class. The Richmond and Scottsville waters also did not check as perfectly as was desired. Further study must be made of these waters.

TABLE 1A

Table showing comparison of observed values and values obtained through use of theoretical curves plotted from formula

PLANT	RAW						COAGULATED						FILTERED						REMARKS
	Alkali		CO_2		pH		Alkali		CO_2		pH		Alkali		CO_2		pH		
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	
Alexandria...	11.0	12.0	4.0	3.8	6.80	6.75	10.0	11.8	6.0	5.1	6.6	6.53	10.0	9.8	7.0	7.2	6.45	6.46	
Alexandria...	9.0	7.8	3.5	4.1	6.65	6.72	11.0	12.3	4.0	3.5	6.8	6.74	10.0	10.3	3.0	2.8	6.85	6.83	
Alexandria...													11.0	10.0	5.0	5.5	6.6	6.65	Soda ash added to filter effluent
Clinchfield...	80.0	77.0	44.0	46.0	6.55	6.57	70.0	70.0	36.0	36.0	6.60	6.60	60.0	57.0	46.0	48.3	6.40	6.42	Mixture of creek and deep well water
Danville.....	22.0	25.5	1.5	1.3	7.55	7.48	10.0	9.8	7.0	7.2	6.45	6.46	12.0	11.0	5.0	5.5	6.65	6.69	No soda ash used. Good floc
Danville.....	16.0	17.3	2.5	2.3	7.15	7.11	13.0	12.2	5.0	6.2	6.7	6.72							Soda ash used = ¼ alum. Good floc
Danville.....	16.0	17.3	2.5	2.3	7.15	7.11	32.0	41.0	1.5	1.2	7.75	7.63	No coagulation—too much soda ash.						Floc probably peptized
Danville.....	16.0	17.5	2.5	2.3	7.15	7.12	5.0	5.0	10.0	10.0	6.0	6.0							Dead floc—opalescent effluent. No soda
Danville.....							17.0	21.5	3 5	2.75	7.10	7.00							
Franklin.....	15.0	15.0	3.0	3.0	7.0	7.0	3.0	3.6	7.0	6.0	6.0	5.92	3.0	3.6	7.0	6.0	6.0	5.92	Organic water-color = 90 Alum only used with improved coagulation. Soda ash to be added to filter effluent
Lynchburg...	9.0	9.3	3.0	2.9	6.8	6.79	8.5	8.7	4.0	3.8	6.65	6.64	8.5	8.7	4.0	3.8	6.65	6.64	Soda ash used in coagulation. Good floc
Monroe.......	10.5	12.0	2.5	2.2	7.0	6.93	8.0	6.8	3.5	4.2	6.60	6.67			See section B				
Orange.......	9.0	10.3	1.5	1.3	7.15	7.09	7.0	6.3	10.0	11.2	6.10	6.15	8.0	8.5	3.5	3.3	6.7	6.67	Soda ash used = ⅓ of alum

Petersburg...	31.0	29.5	3.0	3.2	7.30	7.32	22.0	22.0	9.0	9.0	6.70	6.70	23.0	19.8	8.0	9.3	6.70	6.77	No lime used
Petersburg...	30.0	29.5	3.0	3.1	7.30	7.31	21.0	17.6	7.0	8.3	6.70	6.78	21.0	19.5	7.0	7.5	6.75	6.79	No lime used
Petersburg...													18.0	16.5	6.0	6.5	6.75	6.78	
Petersburg...													28.0	28.2	4.0	4.2	7.15	7.16	0.12 g.p.g. lime added to filter effluent
Petersburg...	40.0	34.0	3.0	3.6	7.35	7.43						See section B							
Petersburg...			See section B				33.0	30.0	6.0	6.7	7.0	7.05			See section B				
Petersburg...			See section B				33.0	31.5	5.0	5.4	7.1	7.12			See section B				
Petersburg...			See section B				16.0	13.5	7.0	8.3	6.60	6.67							
Richmond...			See section B				23.0	26.5	8.5	7.5	6.80	6.78							
Richmond...			See section B				26.0	22.0	5.5	6.6	6.90	6.98			No filters				Alum only. Purification by setting.
Richmond...			See section B				25.0	24.5	5.5	5.7	6.95	6.97							
Richmond...			See section B				18.0	19.5	8.0	7.3	6.70	6.66							
Richmond...			See section B				6.0	6.2	10.0	9.7	6.10	6.08							
Scottsville....			See section B				35.0	27.5	5.0	6.3	7.05	7.15	38.0	39.5	4.0	3.8	7.30	7.28	
Scottsville....			See section B						See section B				38.0	37.5	3.0	3.1	7.4	7.41	Soda ash added to filter effluent
Suffolk.......	10.0	12.2	5.0	4.8	6.7	6.61	4.0	4.3	8.0	7.25	6.05	6.01	4.0	4.3	8.0	7.25	6.05	6.01	Lime and alum in coagulation. Color R. W. 120
Suffolk.......	10.0	12.2	5.0	4.8	6.7	6.61	4.0	3.95	8.0	8.15	6.00	6.01	4.0	3.95	8.0	8.15	6.0	6.01	Alum dose reduced. No lime
Suffolk.......	10.0	12.2	5.0	4.8	6.7	6.61	3.5	3.5	7.0	7.0	6.00	6.00	4.0	4.2	7.0	6.4	6.10	6.06	Alum further reduced. Good floc
Suffolk.......	10.0	12.2	5.0	4.8	6.7	6.61	2.0	2.0	8.0	8.0	5.7	5.7	2.0	2.2	7.0	6.4	5.8	5.77	In determination of CO_2 some error due to organic acids

TABLE 1B

Table showing comparison of observed values and values obtained through use of theoretical curves plotted from formula

PLANT	RAW						COAGULATED						FILTERED						REMARKS
	Alkali		CO_2		pH		Alkali		CO_2		pH		Alkali		CO_2		pH		
	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	Observed	Calculated	
Alexandria...	11.0	15.5	5.0	3.5	6.8	6.65	3.5	5.6	9.0	5.7	6.1	5.88	3.5	5.6	9.0	5.7	6.1	5.88	Explanation not known
Bedford......													5.0	7.6	3.5	2.3	6.65	6.47	Explanation not known
Bedford......													5.0	9.5	3.0	1.6	6.8	6.53	Explanation not known
Hopewell.....	47.0	30.0	3.0	4.8	7.30	7.50													Explanation not known
Monroe.......							See section A						9.0	5.0	2.5	4.5	6.6	6.87	Explanation not known
Norfolk.. ...	22.0	43.0	7.0	3.5	7.10	6.80	6.0	13.2	19.0	8.60	6.15	5.81	7.5	12.7	18.5	10.5	6.15	5.93	Supply to be further investigated
Norfolk......	25.0	17.5	4.0	5.7	6.95	7.10	21.0	18.0	9.0	10.6	6.60	6.68	20.0	15.5	8.0	10.3	6.60	6.71	
Petersburg...	41.0	26.5	3.0	4.7	7.25	7.44	35.0	52.0	6.0	4.5	7.25	7.07	35.0	58.5	6.0	4.5	7.30	7.07	Further study is required to find why so great a proportion of Petersburg fall in section B
Petersburg...			See section A				32.0	17.5	7.0	12.7	6.7	7.03	32.0	14.5	6.0	12.7	6.70	7.03	
Petersburg...	41.0	30.0	3.0	4.2	7.30	7.44			See section A				34.0	24.0	6.0	8.6	6.9	7.06	
Petersburg...	36.0	24.0	3.0	4.6	7.20	7.38			See section A				29.0	22.0	7.0	9.2	6.8	6.93	
Petersburg...	32.0	24.0	3.0	4.1	7.20	7.32	23.0	17.5	7.0	9.3	6.7	6.83	23.0	17.5	7.0	9.3	6.7	6.83	
Petersburg...	26.0	16.0	1.5	2.3	7.35	7.55			See section A				18.0	13.5	7.0	9.1	6.6	6.72	
Petersburg...													23.0	14.5	6.0	9.3	6.7	6.9	
Richmond...	41.0	27.0	1.75	2.60	7.5	7.66			See section A						No filters				0.75 CO_2 error in raw = 14 p.p.m. alkalinity
Richmond...	23.0	44.0	4.0	2.2	7.35	7.07			See section A						No filters				Turbid raw water possibly gave false pH
Richmond...							16.0	12.5	8.0	10.3	6.50	6.62			No filters				Quality of water similar to Petersburg. Requires further study,
Scottsville....	33.5	17.0	1.5	3.15	7.35	7.67							See section A						Calculated results inaccurate because of low CO_2

TABLE 2

Showing various plants and per cent of tests satisfactory (section A) compared with per cent tests unsatisfactory (section B)

	NUMBER OF TESTS IN SECTION		PER CENT OF TESTS IN SECTION	
	A	B	A	B
Alexandria	7	3	70	30
Clinchfield	3	0	100	0
Danville	10	0	100	0
Franklin	3	0	100	0
Lynchburg	3	0	100	0
Monroe	2	1	66	33
Orange	3	0	100	0
Richmond	5	3	63	37
Scottsville	3	1	75	25
Suffolk	12	0	100	0
Bedford	0	2	0	100
Hopewell	0	1	0	100
Norfolk	1	5	17	83
Petersburg	12	15	44	56

95 tests made, 62 in section A = 65 per cent, 33 in section B = 35 per cent.

pH DETERMINATIONS IN THE SMALL PLANT

In view of our experience we have concluded that the present standards available on the market are not sufficiently satisfactory to warrant recommendation of their purchase and use in the smaller plants. Except under certain conditions, as previously pointed out, pH observations and calculated CO_2 are more preferable than observed CO_2 and calculated pH. The pH test is simple and rapid. The apparatus is compact and is readily transported from place to place. The chief objection to standards prepared from buffer-solutions and organic dyes is their lack of stability for a sufficient period. They are relatively expensive and the tubes fragile because of the thin tips of the ampules. In larger plants where a chemist is in charge, all objections are minimized somewhat because of the relative ease with which new standards may be prepared when necessary. In the small plant we are afraid that the failure of the standards or the loss of some of the series might lead to undesirable results or might do injury to a method with an apparent future usefulness. It is highly desirable that permanent standard color solutions be prepared for such use. Perhaps some day the operators will be able to purchase a series of color solutions made from inorganic compounds. These solutions could be supplied in stock-bottles with each of a definite pH value. Empty tubes with stoppers furnished could be filled or refilled from the stock bottles as often as required. A broken standard tube could be then quickly replaced in the series by the operator. The organic dye solutions used as indicators in the water-sample tested are not subject to appreciable deterioration when kept in a dark cool place.

After four weeks of use by the authors a material change in certain of our pH standards has been observed. Methyl red standards lost their color completely within two weeks after purchase. The brom-thymol blue standards are more satisfactory than those prepared from phenol red. It is fortunate that the pH zone for most coagulated waters is covered by the brom-thymol blue series.

We understand that at least one investigator, Geo. C. Bunker of Panama, is working along lines toward the preparation of permanent pH standards. A great aid to all concerned will result if he is successful in producing them.

The relative ease and accuracy of pH observations and the comparative difficulty and "vanishing" end point of the CO_2 titration, together with the relative accuracy of calculated CO_2, will warrant the displacement of CO_2 titration by pH observations by many at present and by all when permanent standards are available. The value of pH observations as applied to filter plants is considerable in this one phase, even though it might never have been suggested as a means of coagulation control. Our thoughts at present are that, in the future, the operator will control coagulation through pH and alkalinity observations. If alkali is added to the filter effluent to reduce "aggressivity," then such a procedure is controlled preferably by titrating the free CO_2 and disregarding the pH and alkalinity except as a matter of interest or for investigative purposes.

The following control test is being used by certain plants in Virginia that are adding soda-ash or lime to the filtered water at a point near the pump suction.

Test: One hundred cubic centimeters of pump discharge to which 10 drops of neutral phenolpthalein solution has been added should show a slight pink cast or require not more than 4 drops (0.2 cc.) of N/22 sodium carbonate solution to produce a slight but visible pink.

Since the institution of this treatment and control a material improvement has resulted in the quality of water at the hot-water services. The limit of 2 p.p.m. CO_2 in delivered water was chosen because of practical reasons and economy of treatment. It may be permissible to allow as much as 3 or 4 parts of CO_2 in certain filtered waters without ill effect. On the other hand, we may find certain waters which will not be so satisfactory even though only 1 or 2 p.p.m. of CO_2 exists. This is a matter which requires further observation and investigation before a report of definite conclusions may be made. The operators are convinced, however, that since the application of alkali to filtered-water was begun consumers have remarked on its improved qualities. Carbon-dioxide removal by alkali has "come to stay" at these plants. As for cost, a plant reducing 6 parts of CO_2 to 2 parts in the filtered water is doing it at a cost of one quarter of a cent per 1000 gallons, where soda ash is employed. Lime would be more economical but not capable of the same ease of application and control and also a slight opalescence is apt to appear in the treated water as the result of the use of an inferior product.

In studying the alum requirements for proper coagulation in two different plants, it was possible to reduce the alkali dose in the raw water. After doing so the alum dose was lowered gradually until the minimum dose producing a satisfactory "floc" was had. In one instance the pH of the coagulated water was reduced through this procedure from pH, 7.3 (that as found) to 6.8 at which the most satisfactory coagulation resulted. In the other case the alkali was eliminated entirely from the raw-water. The alum dose was then reduced with resulting improved quality of "floc." The pH resulting after alkali elimination and alum reduction was the same as that found originally, 6.1. The latter was a highly organic water receiving aeration subsequent to alum addition.

Of economic importance is the saving at each of these plants of over $200.00 per month.

ALUMINUM COMPOUNDS IN FILTER EFFLUENTS

During the investigation no tests were made for aluminum compounds in the filtered water. It has been known to the authors since 1919 that a positive test for alumina, when using the haematoxylin or log-wood extract color tests, is obtained on many filter effluents. This is particularly true of waters which have had alkali applied to produce a low CO_2 content prior to filtration, regardless of the point of application of the alkali. Alumina in combination will reach a minimum in effluents where the coagulation is most nearly perfect. Where the alum dose is properly controlled and added alkali is not allowed to exceed a dose sufficient to produce a coagulated-water of an alkalinity of more than 5 parts less than that of the raw water, the coagulation will be satisfactory. The colorimetric alumina test has not proved very satisfactory as a quantitative procedure. We felt that after the coagulation had been made as satisfactory as possible no considerable advantage would result from a determination of the aluminum compounds in the effluent. In this day of widespread use of aluminum cooking utensils we are wondering what ratio the aluminum eaten in food bears to the aluminum which would be obtained through the water imbibed by the same person, assuming the water to contain as much as 0.2 p.p.m. of aluminum, this quantity being the maximum ever found by one of the authors previous to this investigation in a treated water where a normal-carbonate alkalinity of 3 to 8 p.p.m. existed in the applied water at the filters.[5] Another reason for avoiding a discussion of the physiological effect of alumina in water is the following. A certain Virginia city is supplied with water purified by coagulation and settling alone. The settled water during most of the time contains traces of aluminum hydroxide and perhaps other compounds of alumina. At times of heavy draught on the plant this amounts to considerable and is visible to the naked eye. Although the water has been blamed by the medical profession for a multitude of disorders, we have not yet heard of a specific ailment

[5] Since preparing the paper for publication, George C. Bunker of the Panama Canal Zone reports to the authors the following experience: A certain plant treating a highly organic and colored water, where a normal carbonate alkalinity (pH about 8.4) has been maintained in the past in the applied water, has been found to give a filter effluent containing as much as 1 p.p.m. aluminum (equivalent to 12 p.p.m. filter alum). The alum has been completely eliminated from the effluent by the following procedure: No alkali is added after floc is formed or until the applied water has passed through the filters. Soda ash is added to the raw water prior to aeration and alum addition, in the proportion of $\frac{1}{3}$ to $\frac{1}{4}$ as much soda ash as alum required to remove the color, etc. The hydrogen ion concentration of the resulting applied water was thereby held closely to pH 6.8. The high CO_2 content was partially removed by the filters, a costly but apparently a justifiable procedure. The remaining CO_2 was absorbed by the addition of lime to the filter effluent, raising thereby the pH to 8.

attributed to the presence of aluminum, although as a general rule doctors advise use of spring-water for babies. The authors would not desire to pass on the value of a treated water containing alumina, in comparison with the famous alum-springs which are reputed to have certain therapeutic value.

CONCLUSIONS

1. The adoption of pH observations is advisable for the larger plants at present and will be for the smaller plants as soon as satisfactory permanent standards are available.
2. For practical purposes the Tillman formula may be used to calculate pH, CO_2 or alkalinity, where two factors are observed and the third is calculated. The formula does not hold when the alkalinity exceeds 65 parts for each part of free CO_2 present.
3. Satisfactory plant control may be had without direct pH observations, but observed or calculated pH will at times be of advantage and is more easily obtained by observation than by calculation.
4. Waters requiring artificial alkalinity should be carefully treated to produce an alkalinity of the coagulated water, at least 3 to 5 parts less than that of the raw later or a pH value of from 5.7 to 7, depending upon the nature of the water.
5. Carbon dioxide in treated waters should be reduced to 2 p.p.m. before pumping into mains, unless the alkalinity exceeds 100. Carbon dioxide reduction should be effected *after* filtration by aeration or by absorption by alkali.
6. Improved coagulation on certain classes of waters requires something in addition to the proper pH zone in which to coagulate. This "something" is obtained by mixing into the water, to which alum has been added, a foreign substance, preferably an insoluble finely ground material having sharp edges. Perhaps the electrical equilibrium of the colloidal phase is destroyed by the sharp edges.
7. Waters of high alkalinity possibly may be more effectively and economically coagulated if the pH is lowered through acid or CO_2 addition to the raw water simultaneously with the alum. Further investigation on this aspect is planned.
8. Waters of various bi-carbonate alkalinities and zero CO_2 will have the same pH value, which was 8.1 according to standards available.
9. Theoretical values for alkalinity, CO_2 and pH have not checked as satisfactorily with observed values at several plants as is desirable.

Further study is necessary to learn the explanation for these discrepancies.

10. A study should be made along lines of the "aggressivity" of filtered waters. Practical experiments on a larger scale than laboratory tests should be carried out to determine the maximum CO_2 content of waters of various alkalinities which will not produce "red-water" in the mains or hot-water services. The results of such a study will be of considerable practical value to water-works superintendents.

The authors have found through laboratory experiments that a certain non-organic raw-water with a pH 7.4, CO_2 of 1.5 parts and alkalinity of 26 was corrosive in the cold under atmospheric pressure. The same water after filtration and the CO_2 reduced by alkali addition to 0.5 parts, the pH raised to 7.7 and an alkalinity of 18 was also slightly corrosive. It is hoped to carry this experimental work further.

11. With improved operation, aluminum compounds need appear in few if in any filtered waters. The extent of the physiological effect of such contents is unknown.

SUMMARY

The writers have attempted an investigation to study the merits of applied pH at filter plants. As a result many interesting facts have been brought out. The facts have been presented for what they are worth with the hope that others may do likewise and mutual benefit may result therefrom. A chart for obtaining the pH of a water without the use of the pH test has been presented and its practical value demonstrated. It has been suggested that an insoluble finely ground foreign substance having sharp edges, if added in coagulation, will materially aid "floc" formation in certain waters. It has been suggested that improved coagulation of waters of high alkalinity and low CO_2 content may be had if the pH of the coagulated water is reduced through acid addition or gassing with CO_2 along with the addition of the alum dose.

A practical method of reducing "red-water" troubles has been presented.

The investigation has proved economically fruitful in reducing chemical costs at two plants.

To E. T. Cranch, of the Petersburg plant, J. H. Spurr, of the Alexandria plant and F. O. Baldwin of the Richmond plant, we are grateful for assistance given and coöperation rendered.

To Richard Messer, Chief Engineer of the Virginia State Department of Health, is due the major credit for this paper, in that it was at his suggestion that the study and investigation were made.

Correction: Formula on figure 1 should read as shown on page 379.